NEW MATERIALS FOR INTERMEDIATE BAND PHOTOVOLTAIC CELLS. THEORETICAL AND EXPERIMENTAL APPROACHES.

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ABSTRACT: Density functional theory calculations of certain transition-metal doped semiconductors show a partially occupied relatively narrow band located between valence band and conduction band. These novel systems, containing the metallic band, are called intermediate-band materials. They have enhanced optoelectronic properties which allow an increase in solar energy conversion efficiency of conventional solar cells. We previously proposed III-V, chalcopyrite and sulfide derived compounds showing desirable characteristics to produce the intermediate band of interest inside the band-gap. In order to obtain further intermediate-band material proposals, this work focuses on studing other compounds constituted mainly by tetravalent elements. The first proposal is vanadium substituting Sn atoms in SnS_2, the second one is composed by type II silicon clathrate with two possibilities: vanadium substituting Si and Ag occluded in the intra-crystalline cavities. UV-Vis-NIR spectra of some of these systems experimentally synthesized show an agreement with previous theoretical predictions.
Keywords: intermediate band, quantum modelling, high efficiency, tin sulphide, silicon clathrate, transition element, thin film

1 INTRODUCTION

Nowadays, most used single gap solar cells (SC) have low efficiency, with maximum values ranging around 20%. In the quest of solar cell efficiency improvement, the photovoltaic community has exposed some hypotheses that may be a key to the wide spread obtainment of an enhanced solar cell in the future. Between these hypotheses, a great attention is given to intermediate-band (IB) concept.

The IB concept is based on having a narrow metallic band inside the semiconductor band-gap, which allows the absorption of two extra low energy photons that promotes a second electron-hole pair, increasing the system photocurrent without affecting the voltage. The IB efficiency had been theoretically predicted as high as 63.2% and can be created by doping over the Mott limit a host semiconductor in which the band-gap is around 2 eV[1].

Recently we proposed different doped semiconductors as IB materials. The systems were constituted by partially substituted materials as: GaP [2]-[4], $CuGaS_2$ [5]-[10], and indium thiospinels [11]. The partial substitution in these materials was made by a transition-metal cation having a partially d shell. Some of these IB materials were synthesized and experimental evidences [12] are consistent with previous theoretical predictions [11].

Nevertheless, a feasible method to get IB material is not completely achieved yet. Theoretical predictions, which can increment the IB materials proposals, are a fundamental support to get the solution to the present problem. In agreement with this, we present different tetravalent elements based materials as new IB-SC.

2 THEORETICAL AND EXPERIMENTAL APPROACHES

2.1 Theoretical approach: models and methods

Theoretical systems modeling

The first assembled system is formed by tin disulfide (SnS_2) (Fig. 1), a semiconductor with 2.30-2.56 eV [13]-[14] band-gap which is relatively near the optimum theoretical value found for an IB-SC.

The partial substitution of tin by vanadium (25%) inside tetravalent SnS_2 semiconductor forms a layered structure of $V_2Sn_6S_{16}$ where vanadium and tin have octahedral coordination.

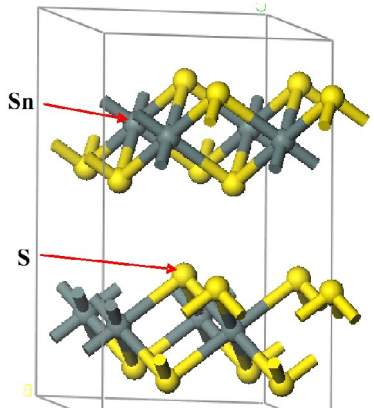
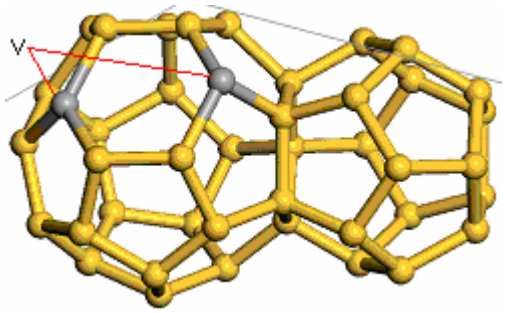


Figure 1: Layered SnS_2 semiconductor structure where Sn and S atoms are labeled.

The second system is constituted by type II silicon clathrate (Si_{34}), a network with 34 tetrahedrally bonded silicon atoms per primitive cell, similar bond as in a regular silicon lattice. This network has a bond topology such that the crystalline structure has internal cavities with 24 or 28 vertices, forming a metastable silicon allotropic phase, with a face-centered cubic Bravais lattice [15]-[17]. The band-gap experimentally found in this material is 1.9 eV [18]-[19], a value that is close to the optimum band-gap theoretically found for an IB-SC. Regular silicon used in photovoltaic applications has a band-gap of 1.1 eV, which is different from the Si_{34} clathrate band-gap.

The two systems proposed are vanadium partially substituted Si_{34} (2 of the 34 atoms in a unit cell) (Fig 2a) and silver occluded inside the largest cavities (Fig 2b).

a)



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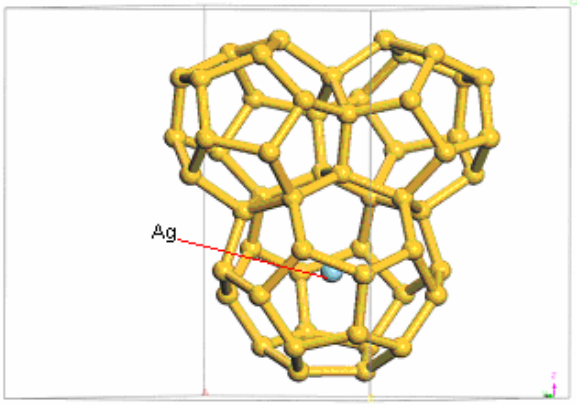


Figure 2: Type II silicon clathrate with a) vanadium substitution b) silver occluded in the larger polyhedral cavity.

Theoretical calculation description

Density functional theory (DFT) calculations, at the GGA level (with PBE functional) and including spin polarization were carried out, with program VASP [20]-[21]. The electronic structure of periodic systems was expanded by the wave-functions in plane waves and represented the atomic core regions with the PAW method [22]-[23]. The expansion cutoff used was high enough to ensure the convergence of all studied materials, and the reciprocal space was sampled according to a dense Monkhorst-Pack grid. In all cases the structures were relaxed in both, atomic coordinates and lattice dimensions, to reach the minimum energy. The obtained relaxed structure was used as a starting point to obtain band structure, density of states (DOS) and projected density of states (PDOS) of the systems.

2.2 Experimental approach: synthesis and characterization

V-substituted SnS_2 was synthesized hydrothermally from aqueous $SnCl_4$ and VCl_3 mixed with thiourea and adding Triton X-100 surfactant to stabilize crystal nanoparticles. The mixture was heated at 175ºC for 48 h in an autoclave and the resulting solid was separated by centrifugation, rinsed with deionized water and methanol and dried in air.

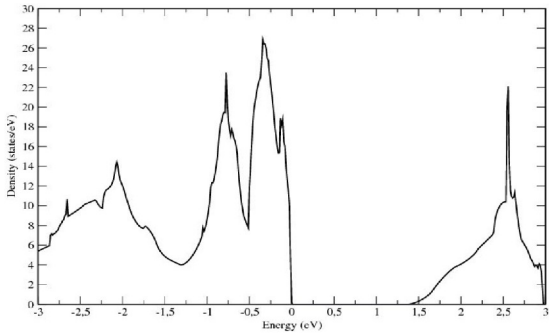
Structural and optical properties of the resulting powders were characterized respectively by X-ray diffraction (DRX) and UV-Vis-NIR diffuse reflectance spectrometry (DRS) .

3 RESULTS AND DISCUSSION

3.1 Intermediate band formation in SnS_2:V system.

$V_2Sn_6S_{16}$ DOS shows an IB which is not present in SnS_2 structure (Fig 3a and Fig 3b). In this system, vanadium 3d electronic orbitals, that mainly form the IB, have t_{2g} symmetry, and consistent with this, three signals of vanadium PDOS appear (Fig 3b). We can also observe that Fermi energy level is located inside the IB.

a)



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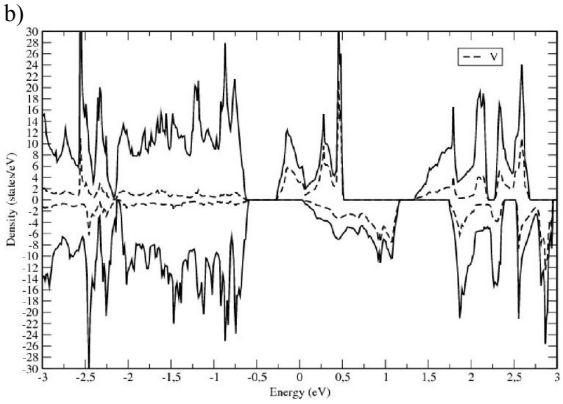

Figure 3: a) DOS of the SnS_2 semiconductor, b) spin up and down DOS (solid line) and vanadium PDOS (dashed line) of $V_2Sn_6S_{16}$. In these figures the Fermi energy level in abscissa is set up at zero.

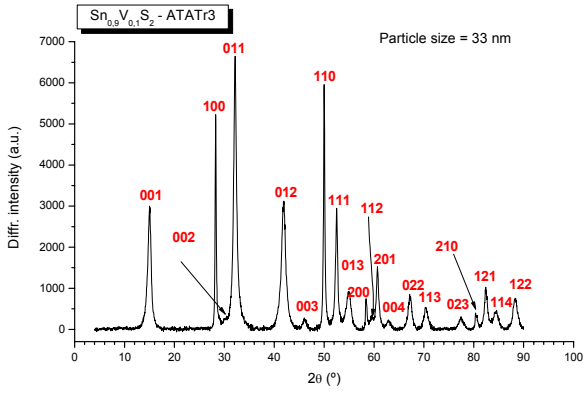

Figure 4: Characterization by DRX demonstrating a mono-phase formation (all peaks correspond to a SnS_2 lattice).

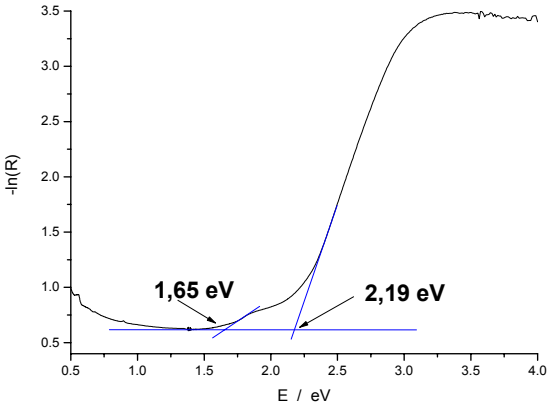

Figure 5: $V_{0.1}Sn_{0.8}S_2$ optical properties characterization with UV-Vis-NIR where we can see two absorption onsets (IB formation is deduced).

DRX experimental characterization of SnS_2:V compound formed by sorvothermal synthesis shows that only a SnS_2 structure is formed (Fig 4). This is demonstrated by the multiple diffracted signals that are the same ones presented in parent semiconductor SnS_2 which means that no other phase is formed and vanadium perfectly substituted tin atoms.

Subsequent UV-Vis-NIR optical spectrum shows two features, one of them corresponding to 2.19 eV which is related to transition of photon absorption by the host semiconductor band-gap (Fig 5) and the other signal corresponding to 1.65 eV. This signal is an experimental evidence of the IB formation.

3.2 Type II silicon clathrate with two vanadium substitutions.

Silicon clathrates are covalent cagelike crystals analogous to fullerene families. When pentavalent vanadium replaces some tetravalent silicon atoms in the Si_{34}, then the whole system exhibits an electron excess.

DOS of V_2Si_{32} shows a spin up IB mainly constituted by 3d orbitals of the tetrahedrally coordinated vanadium (Fig 6). Orbitals with *e* symmetry form the IB, meanwhile orbitals with t_2 symmetry are located at higher energy values. Vanadium PDOS confirms these results.

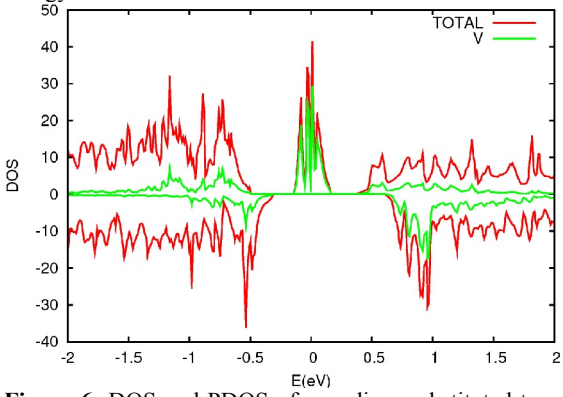

Figure 6: DOS and PDOS of vanadium substituted type II silicon clathrate forming V_2Si_{32}.

Nevertheless, in this system vanadium have a V^{4+} oxidation state, and V^{4+} fundamentally exists in an octahedral environment, e.g. vanadium silicide VSi_2 where Si is 8-fold coordinated to Si [24]. In agreement with this, we expect vanadium substitution in Si_{34} network will not be energetically favored.

3.3 Type II silicon clathrate with an Ag atom occluded in the main polyhedral cavity.

Clathrates, however, provide another alternative, the possibility of occluding guest atoms inside cavities. Group 11 elements have been tested and an IB results when Ag is inserted in the largest cavities.

In the simplest case of Ag occluded in Si_{34} cavities, forming $AgSi_{34}$ system, the lattice contains only one guest atom at zero oxidation state inside the main polyhedral cavity.

No strong covalent interaction between network of clathrate and silver exists. Silver is a noble metal and we expect not to have a big electronic density transfer to or from the Si lattice and silver.

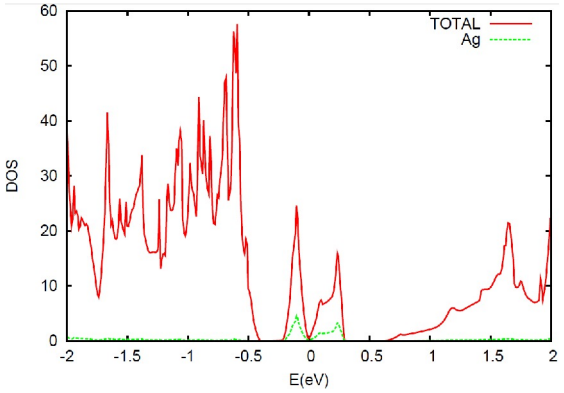

Figure 7: DOS and PDOS of $AgSi_{34}$ that exhibits an IB formation.

In this case, where no bond interactions exist between silver and the clathrate, silver atoms indeed conserve a single electron in an orbital of *s* symmetry which is a partially filled electron orbital that may form the IB at an adequate energy position. The evidence of an IB formation by this structure is depicted in the $AgSi_{34}$ DOS and silver PDOS (Fig 7).

4 CONCLUSIONS

Theoretical calculations and experimental characterization indicate the desired intermediate band materials formation in the proposed systems.

SnS_2 and Si_{34} based intermediate-band materials can be formed by vanadium partial substitution. Silver atoms occluded in the main polyhedral cavity of Si_{34} form a $AgSi_{34}$ structure. This system can also form an intermediate band and is more likely to be realizable than V_2Si_{32} formed by partial substitution of silicon by vanadium.

The experimentally obtained V in SnS_2 material has been synthesized in a polycrystalline form, and can be an optimum system for thin film devices. The resulting intermediate-band systems could be implemented as solar cells with high efficiency.

5 ACKNOWLEDGEMENTS

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